



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/NO90/00115</p> <p>(22) International Filing Date: 11 July 1990 (11.07.90)</p> <p>(30) Priority data: 892925 17 July 1989 (17.07.89) NO</p> <p>(71) Applicant (for all designated States except US): NORSK HYDRO A.S [NO/NO]; N-0240 Oslo 2 (NO).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): RUCH, Wolfgang, Walter [DE/NO]; Bruflata 2, N-6600 Sunndalsøra (NO). KIRKEVÅG, Bjørn [NO/NO]; Børsetlauvet 16, N-6620 Ålvundeid (NO).</p> <p>(74) Agent: RICANEK, Ivan; Norsk Hydro a.s, N-0240 Oslo 2 (NO).</p>	<p>(81) Designated States: AT (European patent), BE (European patent), BR, CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), SU, US.</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: A PROCESS OF MANUFACTURING PARTICLE REINFORCED METAL FOAM AND PRODUCT THERE-OF</p> <div data-bbox="276 1281 1412 1701"> <pre> graph TD     A[Remelting of PMMC material] --&gt; B[Foaming by means of cellulating gas]     B --&gt; C[Accumulation of metal foam on top of the melt]     C --&gt; D[Solidification in moulds]     C -.-&gt; E["(Re)shaping of foam metal"]     E -.-&gt; D     F[Preparation of molten PMMC material] -.-&gt; A           </pre> </div> <p>(57) Abstract</p> <p>Particle reinforced low cost metal foam is provided by a process of manufacturing metal foam based on foaming of molten composite material using finely dispersed cellulating gas.</p>		

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A process of manufacturing particle reinforced metal foam and product thereof

The present invention relates to a process of providing metal foam and more particularly to a process resulting in provision of thin wall close cell particle reinforced metal foam.

Foamed metals, as well as foamed ceramics and plastics, due to their unique combination of properties and light weight are earning growing attention as engineering materials.

There are several ways to produce foams. Different foaming techniques are known such as incorporating hydrides in the molten metal or adding organic compounds which release gases on heating. Vapor deposition on polymeric substrates or casting of metal around granules which are then leached out leaving a porous metal structure are other examples of providing metals with cellular structure.

The process of foam formation using blowing agents is affected by the surface tension and viscosity of the actual melt. The viscosity counteracts bursting of the cell walls during a progressive increase in the volume of the formed bubbles, while a low surface tension will favour formation of thin bubble walls.

The properties of foams being gas-in-solid dispersions are largely determined by their density, but the cell size, structure and their distribution are also important parameters influencing the properties.

In general such foamed metals are produced by adding a gas evolving compound to the molten metal followed by heating of the resultant mixture to decompose the compound and to produce expanding cellulating gases. The foaming compound is usually metal hydride such as  $TiH_2$  or  $ZrH_2$ , and after the foaming step the mould is cooled to form a solid foam material. Cells of non-uniform structure and/or undesirably large size are experienced due to the difficulties with uniform distribution of the evolving gas through the whole volume of the foamed metal.

GB patent No. 1.287.994 discloses a process for preparation of metal foams applying a viscosity increasing agent comprising an inert gas or an oxygen containing material gaseous at the melt conditions and treating the thus produced viscous melt with a foaming agent. Air, nitrogen, carbon dioxide, argon and water are preferably used in the process as viscosity increasing agents in amounts from 1 to 6 grams per 100 grams of metal alloy. Metal hydrides are used as foaming agents (hafnium, titanium or zirconium hydrides) in amounts of from 0,5 to 1,0 grams per 100 grams of alloy.

Preferably the increase in viscosity is enhanced by the presence of a promoter metal, e.g. from 4 to 7 weight% magnesium is used in aluminium alloys. A good mixing technique is required, the addition of foaming agents is usually carried out at a temperature lower than addition of the viscosity increasing agent in a separate second vessel. The disclosed batchwise process, achieving better foams with regard to uniform size and distribution of the cells, and claiming a certain reduction in the consumption of foaming agents, is a rather complicated time consuming and

expensive process requiring several process steps and units based on use of expensive heat decomposable gas evolving compounds (hydrides).

European patent application No. 0 210 803 discloses a similar batchwise method of producing foamed metals based on use of from 0,2 to 8,0 weight% metallic calcium as viscosity adjusting agent and titanium hydride in amounts of from 1 to 3 weight% of the molten melt as foaming agent.

Still another method of producing cellularized metal by decomposition of a heat-decomposable gas evolving compound in molten metal is disclosed in US patent No. 3.297.431. The improvement comprises addition of an intimately dispersed, finely divided powder to the metal prior to decomposition of the gas evolving compound (carbonates or hydrides), or dissolving of gas in the melt. The stabilizing powders may be metals or non-metals, elements or compounds, and two wettable powders are preferentially used where one of which forms a solid alloy with the metal. Usually the gas is dissolved at one pressure and then evolved at a second lower pressure.

A drawback in common for the hitherto known processes is that all of them are batchwise operating processes using either expensive gas evolving compounds or dissolved gases as cellulating means and viscosity increasing or stabilizing additives to achieve quality metal foams.

Furthermore, the prior art processes require a close control with the temperature and pressure conditions at different steps of the process. Consequently, so far there is no method operating on an industrial scale in an economical way offering a low cost metal foam to compete with other engineering materials.

Accordingly, it is an object of this invention to provide a simple low cost method for preparation of quality foams.

Another object of the invention is to provide a method for upgrading of scrap metal material.

Still another object of the invention is to provide a novel type of particle reinforced metal foam having improved mechanical properties.

The invention in its various aspects will be described in details, and various other objects, advantages and additional features thereof will become more apparent from the following description and accompanying patent claims which are to be read in conjunction with the attached drawings, Fig. 1-4, where

Fig. 1 shows schematically in the form of a flow-sheet the process of preparation of metal foam according to the invention,

Fig. 2 displays a natural size contact print of the foamed metal sample prepared according to the invention,

Fig. 3 shows an optical metallograph picture of the closed cell Al-foam structure,

Fig. 4 illustrates graphically results from a compression test conducted on foam samples.

Referring to Fig. 1, illustrating schematically the process of metal foam preparation, it has been found that a metal foam of the closed cell type structure having a uniform density and cell structure can be provided simply by feeding of finely dispersed

cellulating gas into a molten particle reinforced metal matrix composite material (PMMC). No special additives adjusting the viscosity of the melt or particular precautions with regard to the distribution of the cellulating gas bubbles through the melt were required. The gas bubbles rise to the top of the melt and form foam gradually increasing in volume. No tendency to bursting of the foam cells when they reach the melt surface was observed. This indicates a (highly) stabilized surface of the gas bubbles. The upper portion of the foam cake solidifies and can be easily removed. Even foam which is not completely solidified can be removed without changing the cell structure due to the thick consistency of the formed foam. This is a quite important feature of the method according to the present invention, which allows to run the process continuously by transfer of semi-solidified foam to the moulds. There is even a possibility of subjecting the foam at this stage to certain forming operations, something which offers a flexibility with regard to the final shape of the resultant metal foam semiproducts.

#### Example 1

30 kg of an eutectic aluminium alloy (Si12Mg1Ni2,5) was melted in an open crucible. The molten alloy kept at a temperature of 650°C was added silicon carbide particles of an average size of 12 $\mu$ m, and simultaneously CO<sub>2</sub> gas was finely dispersed through the melt by means of a special treatment rotor as disclosed in US patent No. 4.618.427. During the feeding of a CO<sub>2</sub> surplus into the formed molten composite material bubbles started to rise to the top of the melt forming a raising foam layer. The upper portions of the foam solidified with no sign of surface burst.

Fig. 2 shows in natural size a photographic picture of the resultant foam sample removed as the solidified top part of the foam cake. The cross-section of the sample exhibits a uniform distribution of cells having a diameter in the range of from 1 to 5 mm. The density of the sample was measured to 0,2 g/cm<sub>3</sub>.

Example 2

20 kg of scrap PMMC material ( $\text{Al}_2\text{O}_3$  reinforced Al-alloy) was re-melted in an open crucible. Pressurized air was applied as source of cellulating gas in this case, finely dispersed and distributed as described in Example 1.

Also in this case the resulting bubbles gave rise to a foamed structure when they reached the top of the melt in the crucible and were allowed to cool.

The achieved pores (cells) are essentially spherical and closed providing the foamed metal with isotropic properties in all directions, especially with regard to energy adsorption. Metallographic examination of the structure on the samples achieved from Example 1 reveals an extremely thin walled foam structure, as illustrated in Fig. 3. The wall thickness in this metallograph picture, magnification of 20, is in order of the reinforcing SiC particle size approximately  $12\mu\text{m}$ .

The mechanical behaviour of the produced foam is represented in Fig. 4 illustrating the results from the testing of compressive stress conducted on the samples from Example 1. The achieved flat stress/strain curve from the samples having an initial height of 26 mm applying a crosshead velocity of 2 mm/min. is typical for this type of material as long as the cell structure did not collapse completely. The energy absorption of this foam was determined to be 2 kJ/l foam, which is a very favourable value compared to the values reported in literature for commercially provided Al-foams. Obviously, the achieved improved mechanical properties of the resultant foams are a result of a beneficial influence from the reinforcing particles incorporated in the cell walls.

Evidently, the above described novel method of preparation of foamed metals according to the present invention offers several



advantages both with regard to the economics of the process and the characteristics of the resulting foams.

First of all there is an opportunity to run the process continuously by continuous remelting or feeding of molten article reinforced metal material using a variety of available gases as a cellulating gas, e.g.  $N_2$ , Ar,  $CO_2$ , He and even pressurized air, which is normally easily available at low costs.

There are no special requirements to temperatures, pressure or uniform distribution of gas bubbles during the foaming and solidification of the resultant foamed metal. The density and to a certain extent also the cell size are simply controlled by dispersion of the cellulating gas through the melt, preferentially by applying the above special treatment rotor, but also other means ensuring finely dispersed bubbles can be applied. The foam accumulated on the top of the melt can be directly fed into moulds for solidification in desired shapes and dimensions or subjected to a certain grade of deformation/reshaping of the semisolidified foam.

Furthermore, even if it is possible to prepare the molten particle reinforced alloy in a separate process step using an active gas and addition of reinforcing particles prior to applying of the cellulating gas, the biggest potential of the present invention is an up-grading of low grade composite scrap material. This constantly increasing volume of composite scrap today represents a considerable problem since it can not simply be remelted or incorporated to the recycled secondary aluminium.

Claims

1. A process of manufacturing particle reinforced metal foam,  
c h a r a c t e r i z e d i n t h a t  
the process is a continuous process comprising steps of  
providing molten composite metal material,  
feeding of cellulating gas into the melt,  
foaming of the melt and accumulation of foamed metal on the top of the melt, and finally  
removal and solidification of the foamed metal.
2. The process according to claim 1,  
c h a r a c t e r i z e d i n t h a t  
the molten composite material is provided by re-melting of particle metal matrix composite material.
3. The process according to claim 1,  
c h a r a c t e r i z e d i n t h a t  
the composite material is formed in situ in the vessel by adding and distribution of reinforcing particles in the molten metal or alloy by means of an active gas.
4. The process according to claim 3,  
c h a r a c t e r i z e d i n t h a t  
the active gas is CO<sub>2</sub> gas and the particles are refractory particles.
5. The process according to one or more preceding claims,  
c h a r a c t e r i z e d i n t h a t  
the molten composite material is aluminium or aluminium alloy.

6. The process according to claim 1,  
c h a r a c t e r i z e d i n t h a t  
the cellulating gas is air.
7. A close cell particle reinforced metal foam  
characterized by cell wall thickness from 10 to  
20,um comprising reinforcing refractory par-  
ticles.
8. The reinforced metal foam according to claim 7,  
c h a r a c t e r i z e d i n t h a t  
the matrix metal is aluminium alloy reinforced  
by SiC particles.
9. The reinforced metal foam according to claim 8,  
c h a r a c t e r i z e d i n t h a t  
the foam exhibits a compressive strength of 0,2  
kg/mm<sup>2</sup> at a density of 0,2 g/cm<sup>3</sup>.

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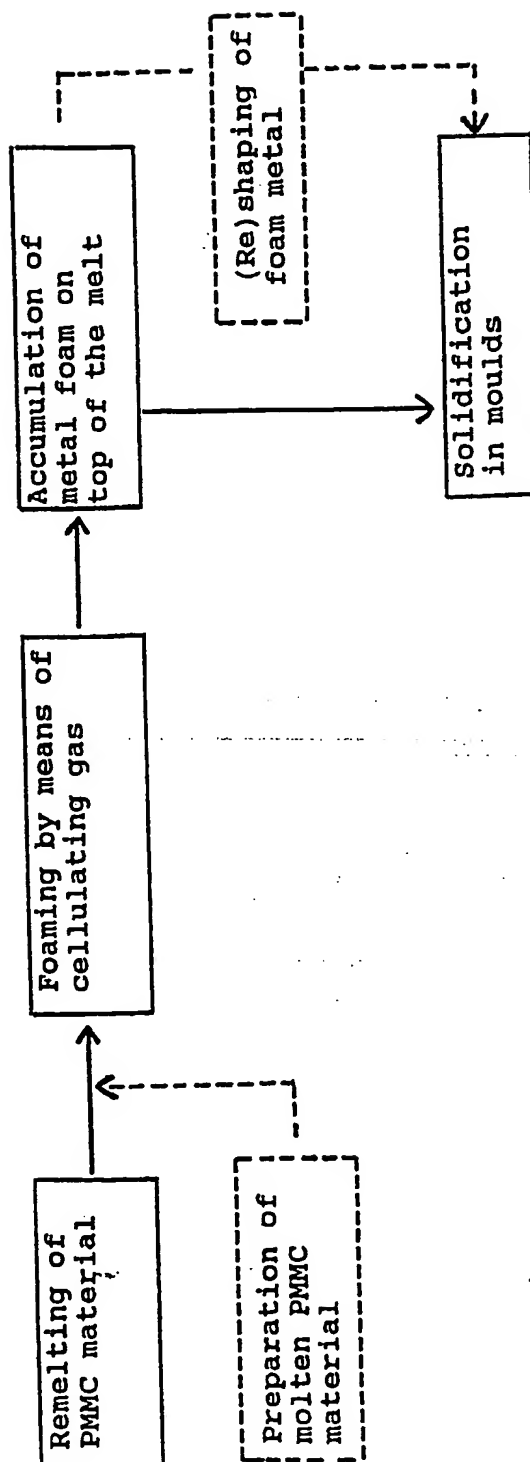


FIG. 1

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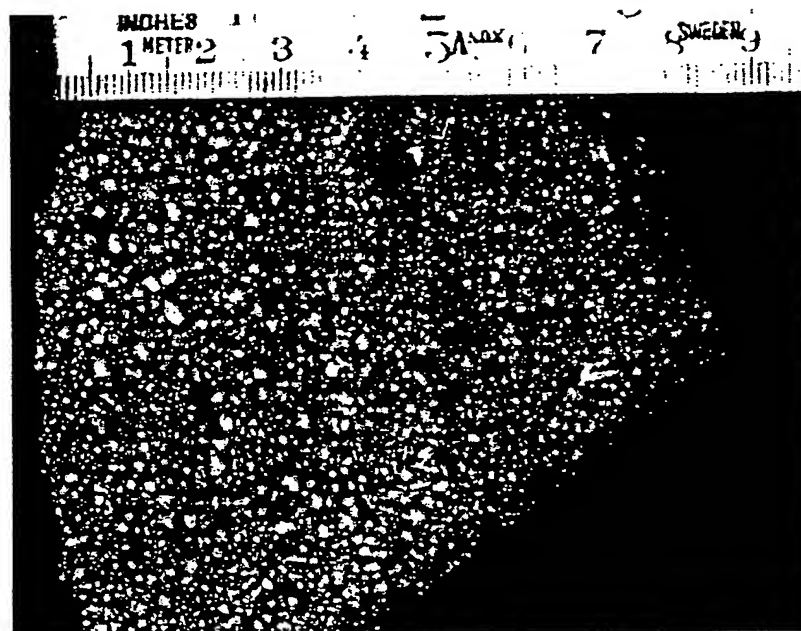


FIG. 2

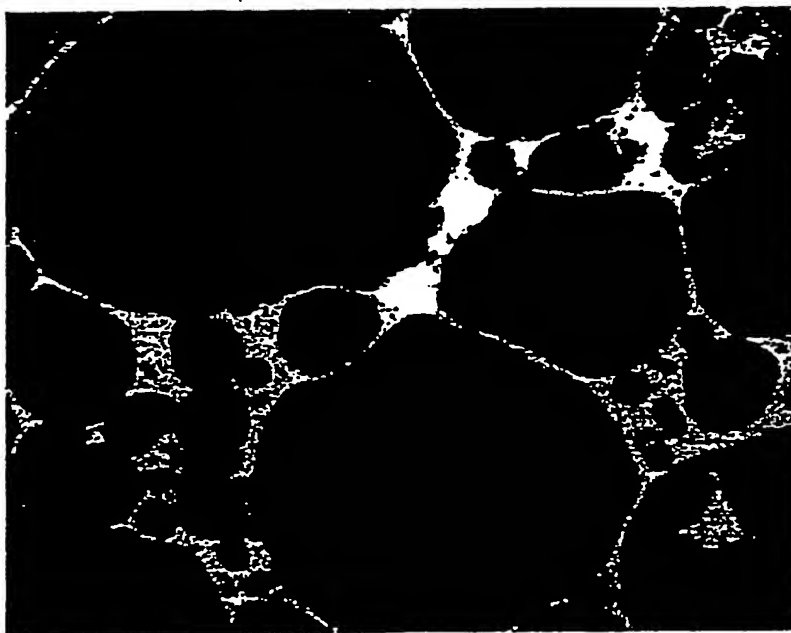


FIG. 3

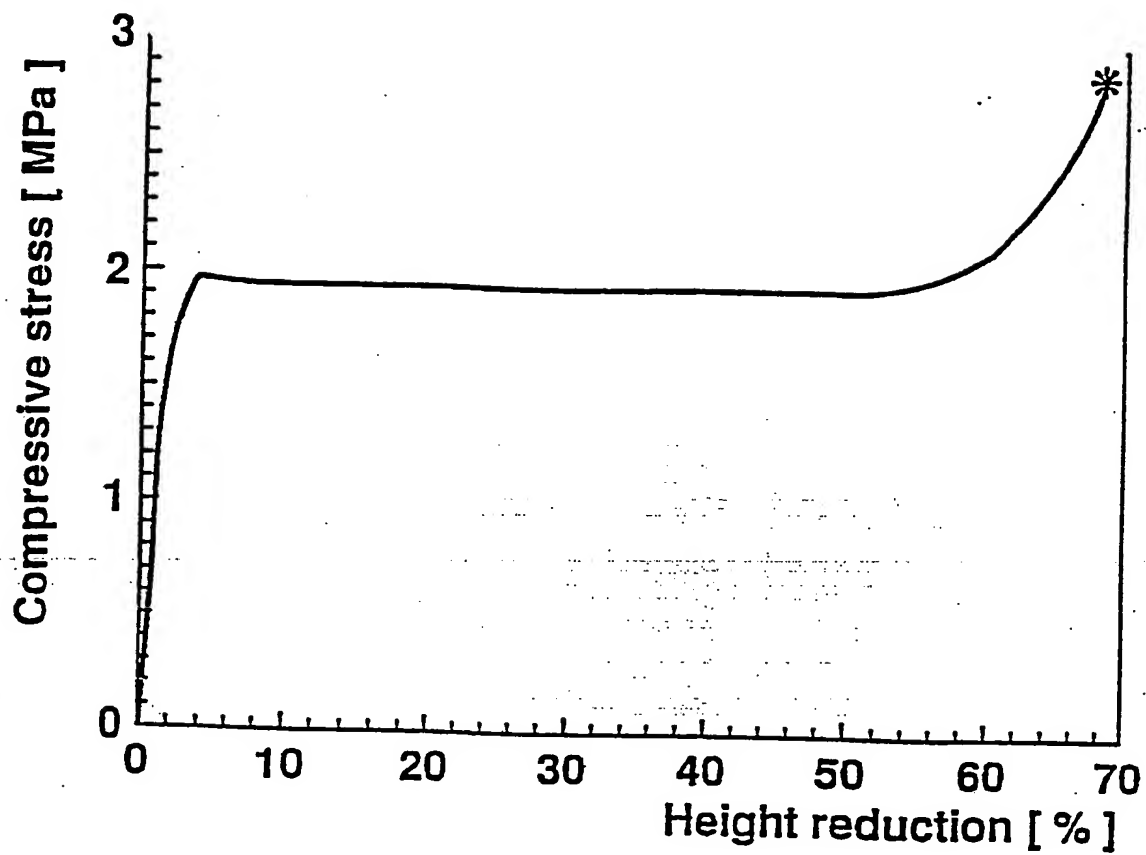
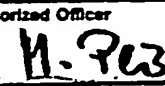


FIG. 4

# INTERNATIONAL SEARCH REPORT

International Application No PCT/NO 90/00115

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>5</sup> : C 22 C 1/08		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
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Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> *		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US, A, 3297431 (J.A. RIDGWAY) 10 January 1967 see claims 3,5; column 2, lines 36-42; column 7, line 73 - column 8, line 37; columns 12,13, example 5; column 15, line 37 - column 16, line 2 (cited in the application) --	1-9
Y	FR, A, 2282479 (PECHINEY) 19 March 1976 see claims 7,8 --	1-9
A	US, A, 3816952 (L.M. NIEBYSKI) 18 June 1974 see claim 1 --	1-9
A	FR, A, 1259163 (LOR CORP.) 1961 see claims 18-20 -----	1-9
<p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
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16th November 1990	- 4. 12. 90	
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ANNEX TO THE INTERNATIONAL SEARCH REPORT  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3297431		None	
FR-A- 2282479	19-03-76	None	
US-A- 3816952	18-06-74	None	
FR-A- 1259163		None	

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